DEVELOPMENT OF AMBIENT TEMPERATURE LITHIUM-ION CELLS

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INTRODUCTION

JPL is involved in NASA Code C sponsored program to develop Li-ion cells for future space applications. The major focus of the program is to develop the basic understanding of the cell chemistry, design and fabricate 5 Ah cells, demonstrate cycle life for LEO and GEO application, and determine safety under inadvertent abuse conditions. The work was carried out so far in the areas of: 1) carbon anode materials, 2) electrode fabrication process, 3) Li intercalation technique, and 4) type of electrolyte and its composition[1-3]. Some of the important findings to this point are: 1) Graphitic carbons were found to exhibit higher reversible lithium capacity compared to coke materials, 2) Ethylene Propylene Diene Monomer (EPDM) is a suitable binder material for the fabrication of carbon electrodes, 3) The two step intercalation technique is effective in realizing the full reversible capacity of carbons compared to the standard one-step method, and 4) EC-based electrolytes are attractive for Li-ion cells. Work is in progress at JPL to evaluate candidate cathode materials for Li-ion cells and fabricate and test experimental cells for technology demonstration. This paper describes the results of the experimental done in these aspects.

EXPERIMENTAL

Expanded nickel metal was used as current collector and substrate for both the graphite anode and TiS_2 cathode. Expanded aluminum metal was used for $LiCoO_2$ cathode. All electrodes were made by a pressing technique. Ethylene propylene diene monomer (EPDM) was used as a binder. Typically, carbon electrodes were coated with 10 - 15 mg of graphite per cm^2, and were 10-15 mil thick. Electrochemical cells were constructed using these electrodes, lithium foil (Foote Mineral Corp.), porous polypropylene separators (Celgard no. 2400), and selected electrolytes.

Mixed (by volume ratio) solvent electrolytes containing ethers and carbonates were chosen for this study. Lithium hexafluoroarsenate

($LiAsF_6$) and Lithium hexafluorophosphate ($LiPF_6$) were used as electrolyte salts. Specifically, the selected electrolytes were: (1) 1.0M $LiPF_6$ in {EC + DEC}, (2) 1.0M $LiAsF_6$ in (EC + 2-MeTHF + DEC) with or without the addition of 2-Methyl furan [2-MeF], and (3) 1.0M $LiPF_6$ in (EC + DMC). The experimental cells were evaluated for charge/discharge characteristics and cycle life. performance. **Constant** current **was used** for charging and discharging the calls. Experiments were conducted in an oxygen and moisture-free dry box.

RESULTS AND DISCUSSION

(1) Li_xC/Li_xTiS_2 Cell Development:

TiS_2 was selected as a candidate cathode material for lithium ion cells initially for the. following reasons: 1) TiS_2 was found to be intrinsically reversible compared to several chalcogenide and oxide cathode materials investigated so far for calls with lithium anodes, 2) the usable specific energy of TiS_2 is about 500 Wh/Kg and compares well with $LiCoO_2$ and $LiNiO_2$, 3) no concluding diluents are needed for TiS_2 cathodes, and 4) charge retention characteristics of lithiated TiS_2 are superior to those of lithiated metal oxides. The low operating voltage is the only known disadvantage of TiS_2 cathode **material.** However, the low operating voltage of the Li_xC/Li_xTiS_2 system (1.4 V ~ 1.9 V) can be considered as an advantage as the cell can be used as a direct replacement for a 1.5 V cell. Hence, in the beginning of this work, it was felt that the advantages of TiS_2 material overweigh **its** disadvantages, and TiS_2 was selected for detail assessment as a cathode material for use in Li-ion cell studies.

Two types of Li_xC/Li_xTiS_2 cells ($C/LiTiS_2$ and LiC_6/TiS_2) were constructed and tested, These calls were activated with 1.0 M $LiAsF_6$ in EC and 2-MeTHF. These two types of cells showed poor cycle life performance. Work is underway to determine the causes for the poor cycle life performance. Some of the preliminary results obtained so far suggest that the poor cycle performance is probably due to: (a) instability of lithiated TiS_2 and lithiated carbon materials in the dry room environment, (b) salt precipitation on the electrode surface during the drying process after the preparation of lithiated carbon and lithiated TiS_2 electrode, and (c) difficulty in cell fabrication. The difficulty of Li_xC/Li_xTiS_2 cell fabrication is due to the complicated handling procedures involving initial preparation of active materials (lithiated TiS_2 or lithiated carbon) in one cell and then transfer of one of these to the final cell. For these masons, the work on Li_xC/Li_xTiS_2 cell fabrication was postponed temporarily. Recently, we have identified a new electrolyte containing 1.0M $LiAsF_6$ in EC + 2-MeTHF + DEC for use in Li_xC/Li_xTiS_2 cells. This new electrolyte has higher conductivity and stability compared to the EC and 2-MeTHF basal electrolyte. The electrolyte was evaluated in the Li/C half cell to determine its long term stabi lity. Cycle life performance of Li/C half cell activated with this electrolyte is given in Figure 1. No capacity fade was observed even after 50 cycles. We intend to evaluate this electrolyte in a Li_xC/Li_xTiS_2 cell at a later date..

(2) Li_xC/Li_xCoO_2 Cell Development :

Work is in progress to evaluate doped and tJII-doped $LiCoO_2$ as a candidate cathode material and understand the parameters that control the cycle life performance of the $Li_xC/LiCoO_2$ cell. Several experimental Li-ion cells are being fabricated to determine the effect of: 1) composition of cathode material, '2) type and composition of electrolyte, 3) electrode capacity ratio, 4) charge cutoff voltage, and 5) cell configuration, on the rate capability, charge retention, and cycle life performance of the cells. 1.0M $LiPF_6$ in EC + DEC was selected as the baseline electrolyte for these studies. Baseline cell design is finalized for these works. These baseline cells have a rated capacity of 250 mAh and are cathode limited in design. These experimental cells have completed 25 cycles with no significant loss of capacity (Figure 2). The results obtained so far validate the suitability of the. baseline design. The results of the testing conducted on the cells of different design will be presented in the paper.

SUMMARY

Experimental $Li_xC/LiCoO_2$ cells, containing electrolyte of 1.0M $LiPF_6$ in EC + DEC, were fabricated and the cycle life testing of these cells is in progress. These cells have a rated capacity of 250 mAh and are cathode limited in design. These experimental cells have completed 25 cycles with no significant loss of capacity. The (difficulty of Li_xC/Li_xTiS_2 cell fabrication is due to the. necessity of cell disassembly and re-assembly. Cell fabrication is being revisited in conjunction with the use of the new electrolyte (1 .0M $LiAsF_6$ in [EC + 2-MeTHF + DEC]).

ACKNOWLEDGEMENTS

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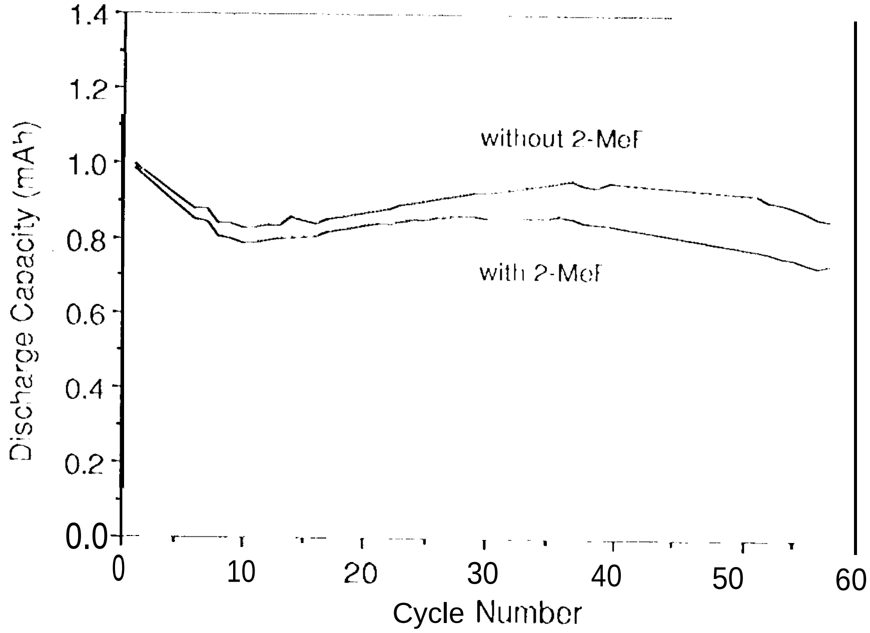

Figure 1. Cycling performance of cells containing 1,0 M LiAsF6 in (EC + 2-MeTHF + EC) with or without the additive 2-MeF.

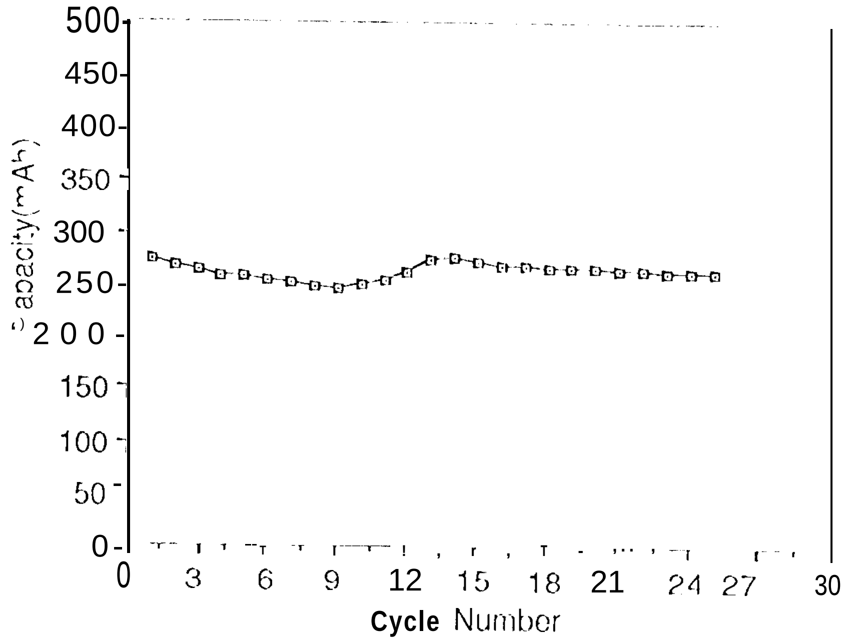

Figure 2. Cycling performance of experimental LixC/LiCoO2 cell.